

Poly- and perfluoroalkyl substances (PFAS), a new class of emerging contaminants

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The environmental liabilities of chlorinated hydrocarbons are long established, and to date other halogens have much less attention from industry. However over the last 18 months, driven by detections in public water supplies and increasing health concerns across the world, perfluorinated compounds are emerging as potentially an even more challenging issue than their Group 7 neighbours.

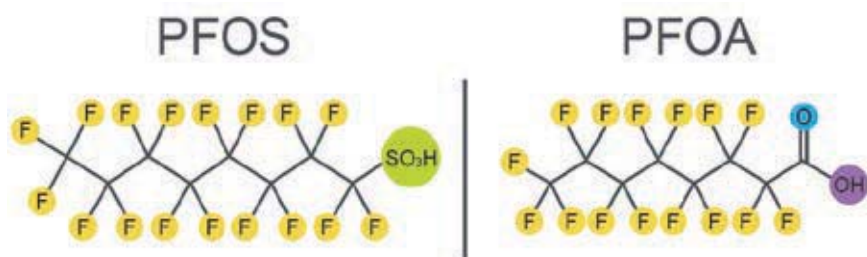


Figure 1: Chemical Structures
PFOS and PFOA

The group of chemicals known as PFAS (poly- and perfluoroalkyl substances) represent a broad class of more than 6,000 compounds and comprise both perfluorinated compounds, where all carbons are saturated with fluorine atoms, and polyfluorinated compounds, where both fluorine saturated carbons and carbons with hydrogen bonds are present.

The unique properties of the fluorine atom, a good stearic mimic for hydrogen but with a significantly different electronegativity gives PFAS compounds a range of desirable properties including resistance to degradation, thermal stability, and unique surface tension and levelling properties which have lead to PFAS compounds being used extensively in a wide range of industrial applications and commercial products.

Primary uses include as stain repellents for textiles and carpeting, non-stick cookware, chromium plating, electronics & photographic industries, water and oil resistant coatings, hydraulic fluids and mist suppressants. They are also major components of the class B (flammable liquid) firefighting foams known as Aqueous Film Forming Foam (AFFF) which have been used in training exercises and fire incidents, most notably at airports, petrochemical and military and civil facilities. This versatility is reflected in the annual production rate which increased significantly from 500 tons/year in the 1970's to almost 5,000 tons/year in 2000^[1].

In the UK concerns around PFAS were first raised immediately after the Buncefield Terminal fire where significant quantities were deployed to land as components of AFFF. The Buncefield Terminal lies above a drinking water aquifer and the Environment Agency introduced a testing regime and temporarily closed abstractions until a risk assessment proved that the drinking water was not at risk from the use of the AFFF

The event did spark interest however and to date

formal regulation two specific PFAS species has been the focus of concern perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) [Figure 1]. PFOS was added to Annex B of the Stockholm Convention in 2009 as a persistent organic pollutant as it is persistent, bioaccumulative and toxic, PFOA was added to the convention in 2016.

The driver behind regulatory scrutiny of PFAS has accelerated in recent years due to concern over the toxicological effects of exposure and bio accumulative throughout the food chain [Figure 2]. Focused mainly on PFOS and PFOA the resulting regulatory standards are unusual as being extremely low; for example, the European Annual Average Environmental Quality Standard for PFOS in inland surface waters is 0.65ng/L.

In the UK, Drinking Water Inspectorate guidance (October 2009) sets out a multi-tiered approach including concentrations for PFOS and PFOA of 0.3µg/L. However, the science on health effects continues to evolve and following review of the latest publications the US Environmental Protection Agency has recently issued Lifetime Health Advisory Limits of 0.07µg/L for total PFOS and PFOA resulting in drinking water significantly below the UK standards and potentially indicating the direction of travel for regulation here. In addition, regulations are developing to over PFAS species in certain US states and in select European countries.

High profile cases of PFAS affecting drinking water supplies have been reported in mainstream media (Time Magazine, Telegraph, New York Times^[2-4]) globally in recent months, associated private & class action *continued on page 18*

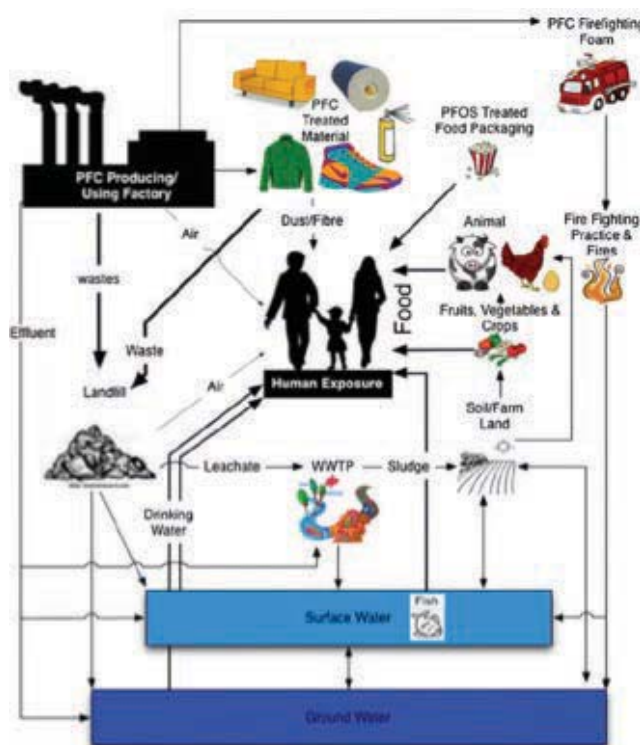


Figure 2: Exposure Pathways PFAS.

Continued from page 15 law suits, and the involvement of celebrity environmentalists such as Erin Brockovich further illustrates increasing levels of concern.

In January 2016, the town of Hoosick Falls, NY, USA, became the first Superfund (Government enforced remediation) site after PFOA was detected in public drinking water wells. This catalyzed testing across the US and multiple other drinking water supplies have been found to be impacted. Globally detections are now reported in drinking water across Europe, Australia, closer to home contamination of the Guernsey water supply from airport AFFF use lead to remedial works and lawsuits^[5].

The scale of the problem may only just be becoming apparent globally as attention is now shifting to focus on a much greater spectrum of PFAS compounds with varying chain length, branching, and functional group which are emerging as a focus of global regulations and raising challenges in terms of analytical chemistry and remediation.

Once in the environment this wide range of compounds degrade through a so called 'biological funnel' in which compounds containing a range of chain lengths and functional groups aerobically biotransform to persistent compounds termed 'dead end daughter' products called perfluoroalkyl acids (PFAAs) which include PFOA and PFDA. These PFAAs are increasingly being regulated as our understanding on toxicology develops [Figure 3].

The PFAAs do not biodegrade, modelling suggests they may have geological scale half-lives due to the strength of the carbon fluorine bond and the lack of naturally occurring perfluorinated compounds meaning microbes capable of breaking them down have not evolved. In this regard they are dissimilar to common organochlorine pollutants such as chloroform and trichloroethene, which have been in the environment over geological time as a result of their emissions from volcanoes, and as such PFAS and PFAAs present a considerable challenge to remediation.

To date analysis of PFAS is limited to less than 40 compounds (including PFOS and PFOA) and does not include the thousands

of precursors (or 'Dark Matter' to be analogous of the 80% hidden mass in the universe) potentially in the environment leading to an underestimation of the problem. To quantify these precursors recent developments use a Total Oxidisable Precursor (TOP) Assay which digests the precursors to form the PFAAs allowing the total range of PFAS to be estimated based on measuring what the resulting increase in PFAAs. This eliminates the need to screen for thousands of PFAS compounds. Arcadis has commercialised this method and is using it to characterise contaminated sites in order that effective risk management strategies and remedial action can be implemented.

In terms of remediating existing contamination typical water treatment responses to address PFAS include using granular activated carbon (GAC), however, sorption levels are generally low, with shorter chain PFAAs being miscible in water and progressively less effectively treated by GAC as the chain length diminishes). Costs for treating water impacted with PFOS and PFOA using GAC are typically 80x more than for the same mass of hydrocarbons such as benzene, but treating the short chain perfluorobutanoates with GAC will not be cost effective due to the very limited sorptive potential. Ion exchange resins and reverse osmosis approaches are also being developed but have challenges around regeneration of resins and management of resulting rejected concentrate.

Destroying PFAS in soils is limited to high temperature incineration (>1,100 °C) which is often prohibitively expensive. Arcadis have recently deployed a new technology to destroy (mineralize) PFAS in situ using a remedial technology known as ScisoR® (Smart Combined In-Situ Oxidation and Reduction).

As with all emerging contaminants this is a fast moving area where uncertainty needs to be managed and understood. Expanded regulatory scrutiny is almost certain and industry will demand appropriate responses are developed cost effectively. ScisoR® technology, is the first of its kind to target PFAS coupled with the TOP Assay makes a powerful analytical and treatment approach and the first holistic solution to the challenges of PFAS. For further information contact Adele. White@arcadis.com.

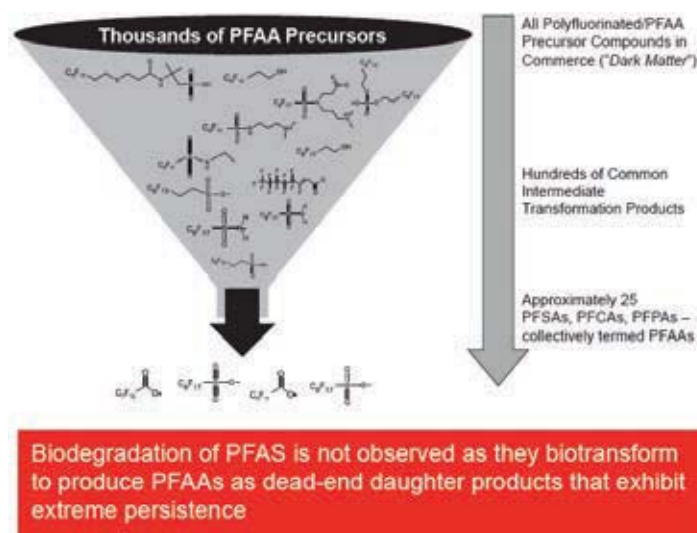


Figure 3: Biological Funnel to Dead End Daughters

Citations

- [1] (*Perfluorooctane Sulphonate (PFOS) Production and Use: Past and Current Evidence* Carloni, 2009)
- [2] *New York Times* 1 January 2016 www.nytimes.com/2016/01/10/magazine/the-lawyer-who-became-duponts-worst-nightmare.html?_r=0
- [3] *Time Magazine* 9 February 2016 <http://time.com/4213091/erin-brockovich-beyond-flint/>
- [4] *Daily Telegraph* 16 January 2016 www.telegraph.co.uk/foodanddrink/foodanddrinkadvice/11643213/Are-we-really-being-poisoned-by-non-stick-pans.html
- [5] *Daily Telegraph* 23 January 2016 www.telegraph.co.uk/finance/newsbysector/industry/12115814/Guernsey-and-3M-in-legal-fight-over-fire-extinguisher-chemicals.html